Neutron Diffraction Study of Pressure-Dependent Magnetism in Molecule Based Magnets

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NCNR

National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Outline

Pressure dependent magnetism

- MBMs and PBAs
- FeCr
- NiCr

FeCr

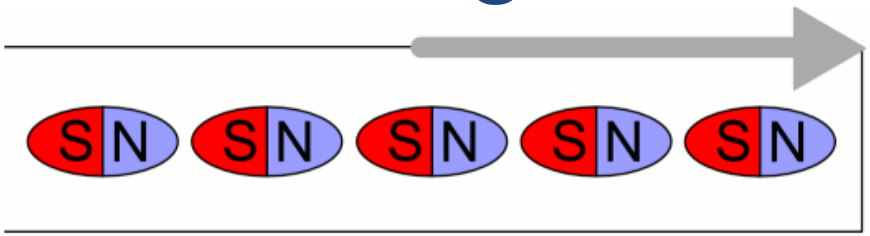
- Synthesis
- First Principles Calculation
- Elemental analysis
- Structural analysis
- Conclusion

NiCr

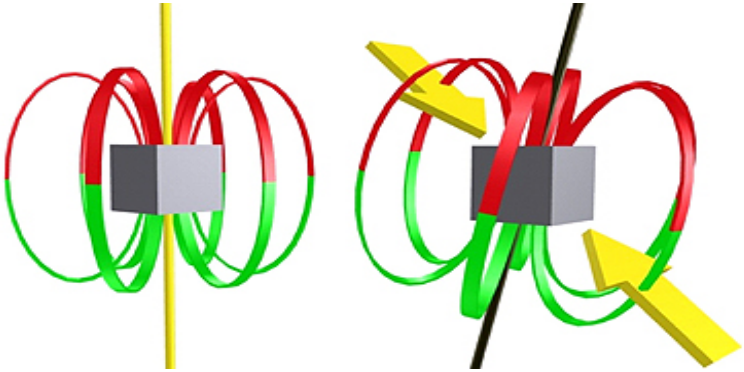
- Synthesis
- First Principles Calculation
- Elemental analysis
- Structural analysis
- Conclusion

The Big Kahuna!

Pressure Dependent Magnetism

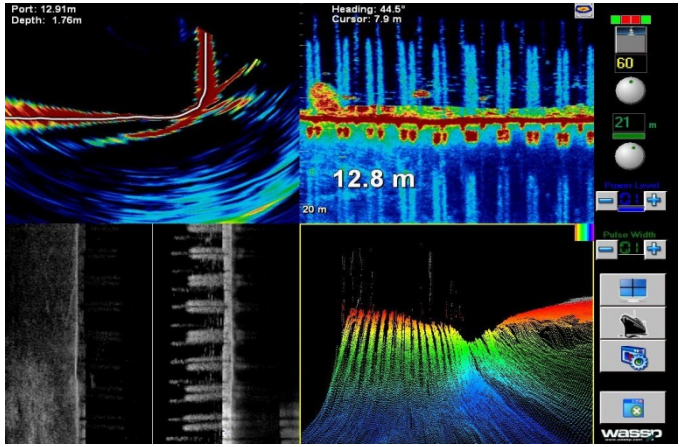


- Magnetostrictive materials



- Villari effect

(inverse magnetostrictive effect)



- Device application: sensor, sonar.

Images taken from Wikipedia, NCTE, and Subseaworldnews.com

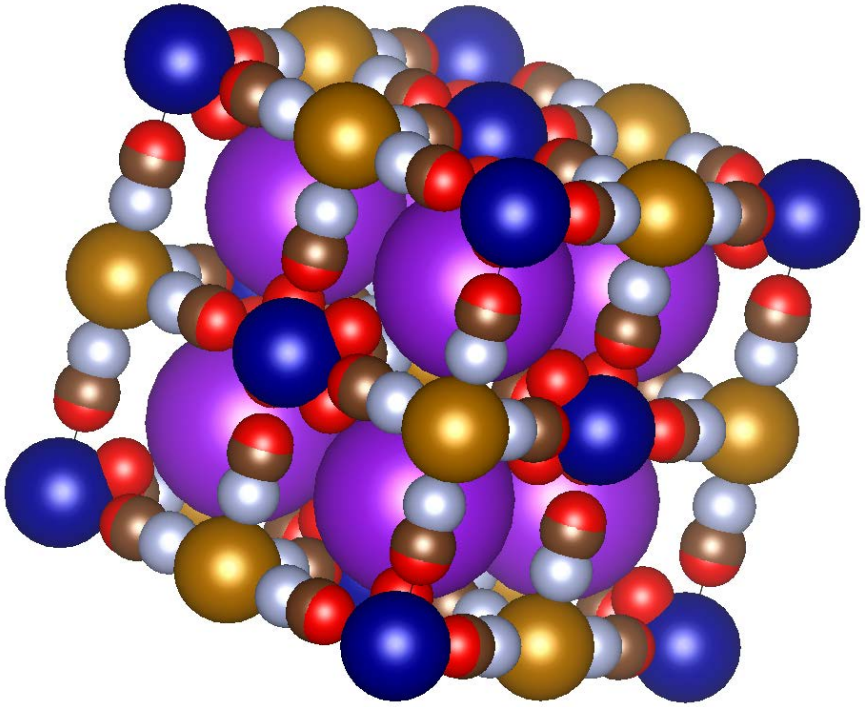
Molecule Based Magnets (MBMs) & Prussian Blue Analogues (PBAs)

MBMs

- Ferromagnetism
- Room-temperature synthesis
- Highly tunable

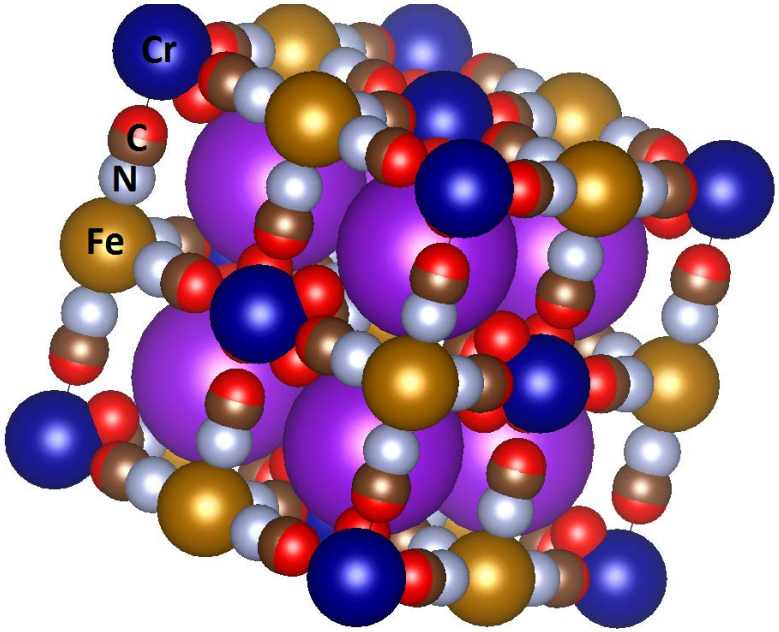
PBAs

- Tunable magnetic ordering
- Mixed valency system
- FCC structure
- $Fm\bar{3}m$ (225)

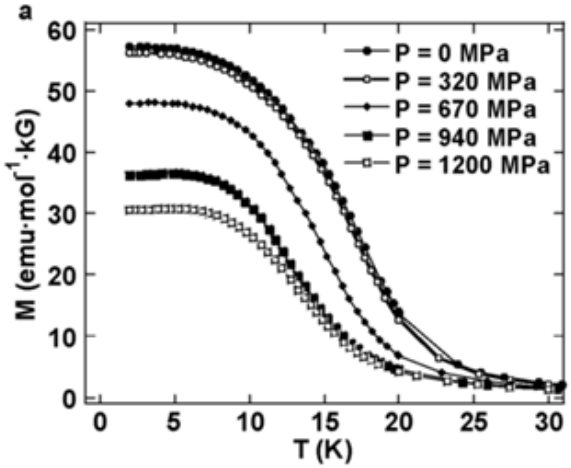


FeCr PBA

- $KFe_3[Cr(CN)_6]_2 \cdot nH_2O$

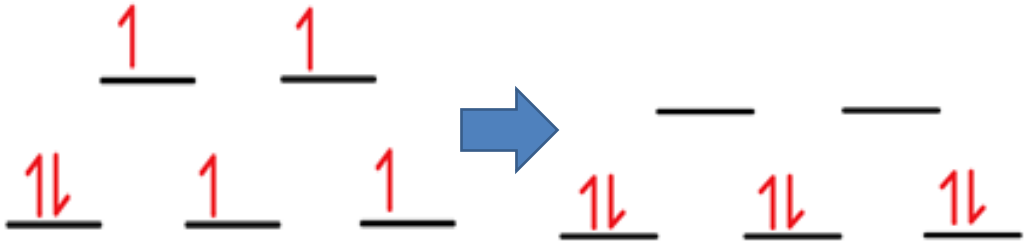


- Magnetization ↓: Pressure ↑



Eugenio Coronado et al. *J. Am. Chem. Soc.* **2005**, 127, 4580-4581.

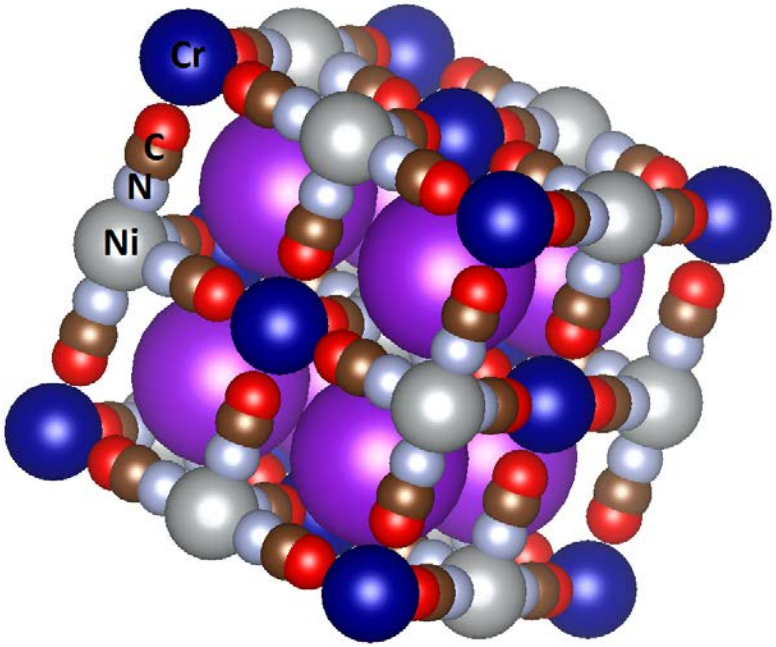
- Hypothesis:
  - Linkage isomerism with spin-crossover (LI)
  - Intrinsic spin-crossover (SC)



S=4 **S=0**

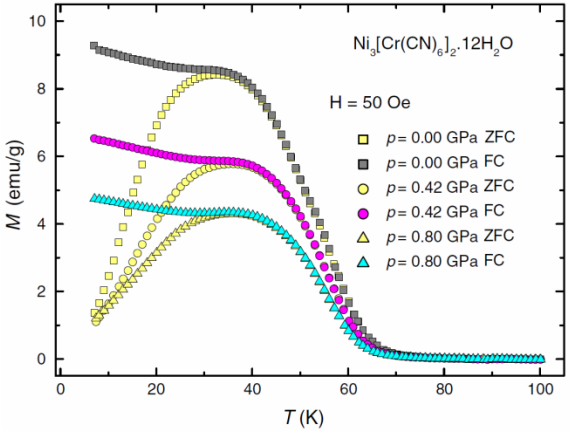
NiCr PBA

- $KNi_3[Cr(CN)_6]_2 \cdot nH_2O$

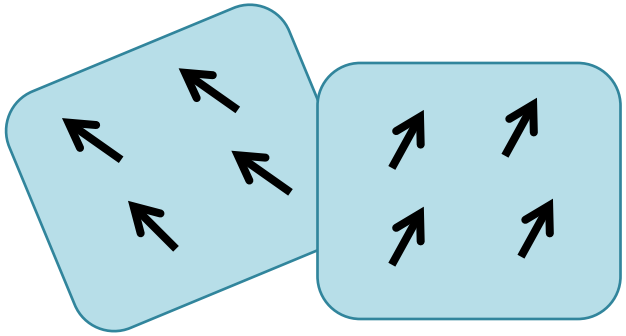


- Hypothesis:
  - LI
  - Random spin-canting
  - Domain wall movement

- Magnetization ↓: Pressure ↑

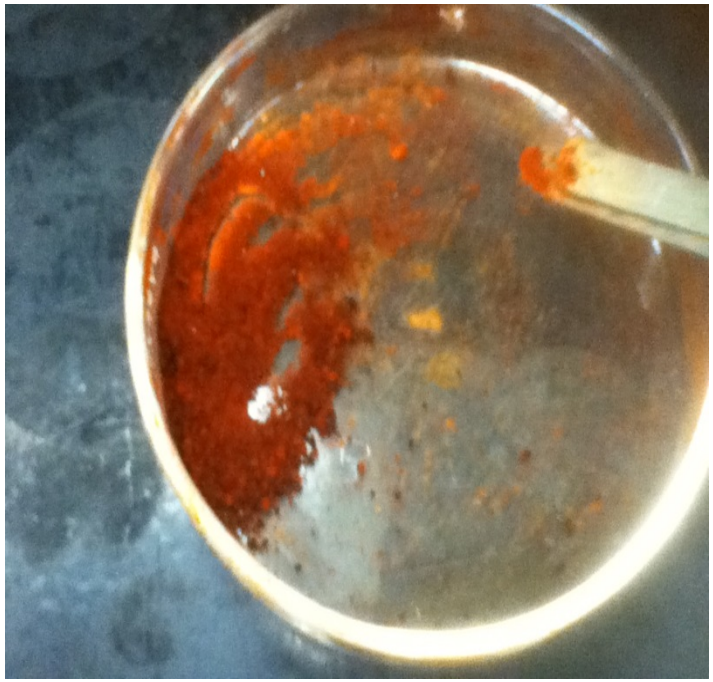


M. Zentkova et al. *J. Phys.: Condens. Matter* **19** (2007) 266217.

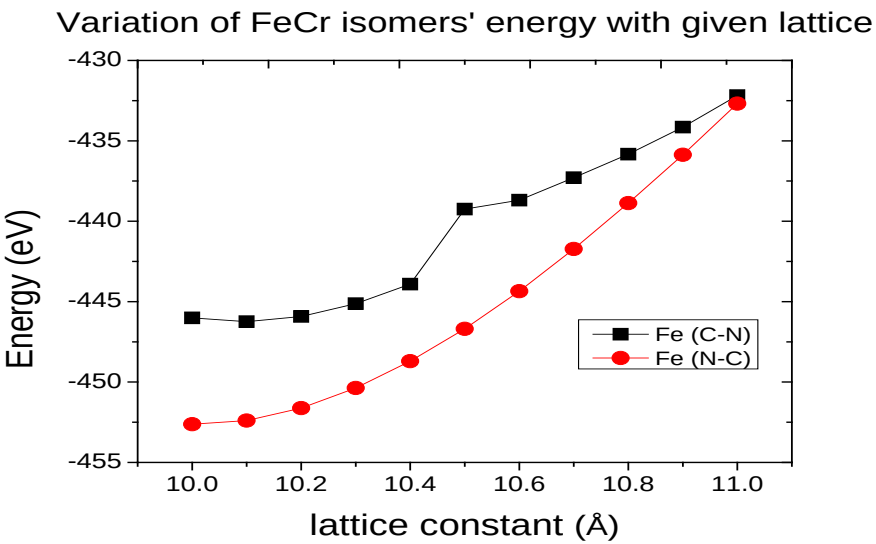


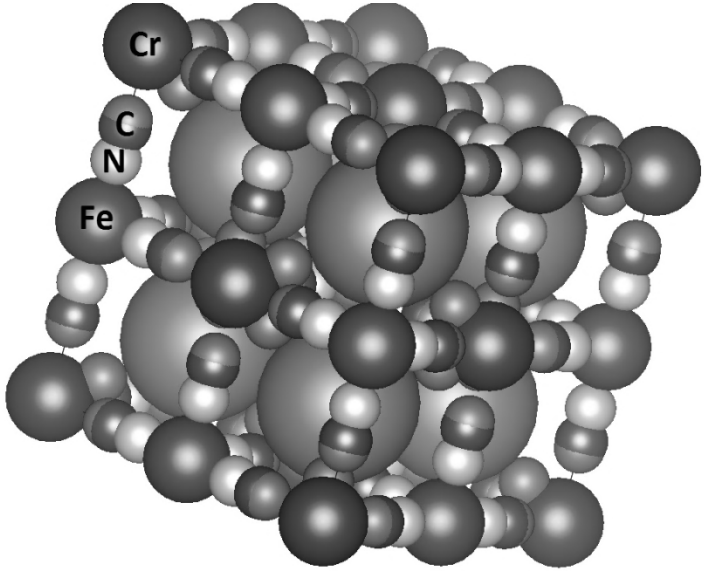
FeCr: Synthesis

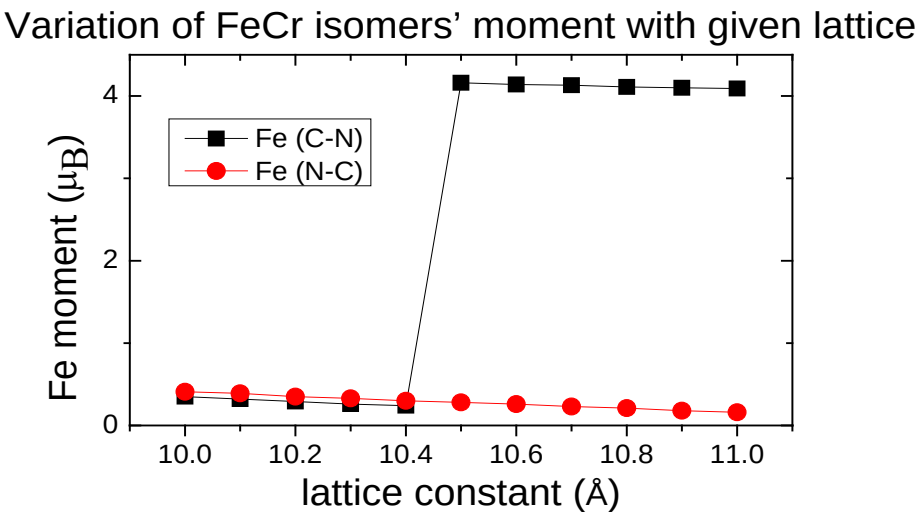
- $K_3Cr(CN)_6$
- $FeCl_2$
- Cold D_2O
- No heat
- Dumped together

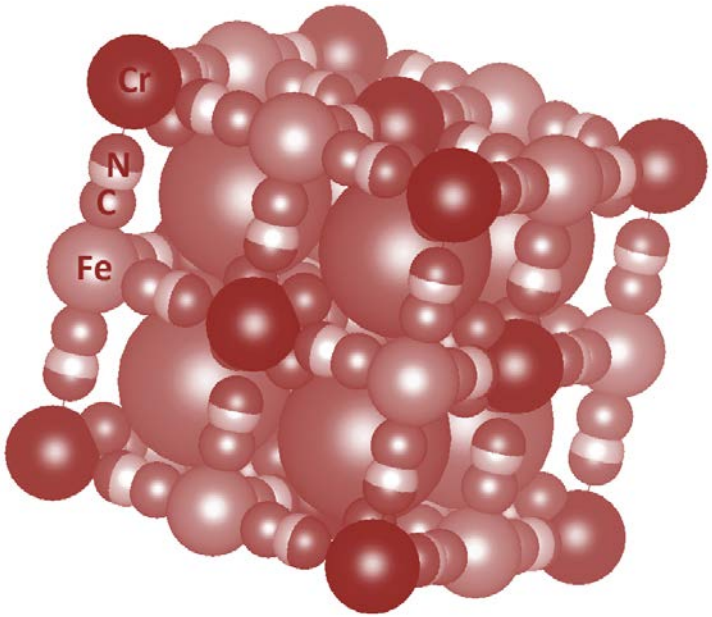


FeCr: DFT


Variation of FeCr isomers' energy with given lattice
Energy (eV)
-430
-435
-440
-445
-450
-455
10.0
10.2
10.4
10.6
10.8
11.0
lattice constant (Å)
Fe (C-N)
Fe (N-C)

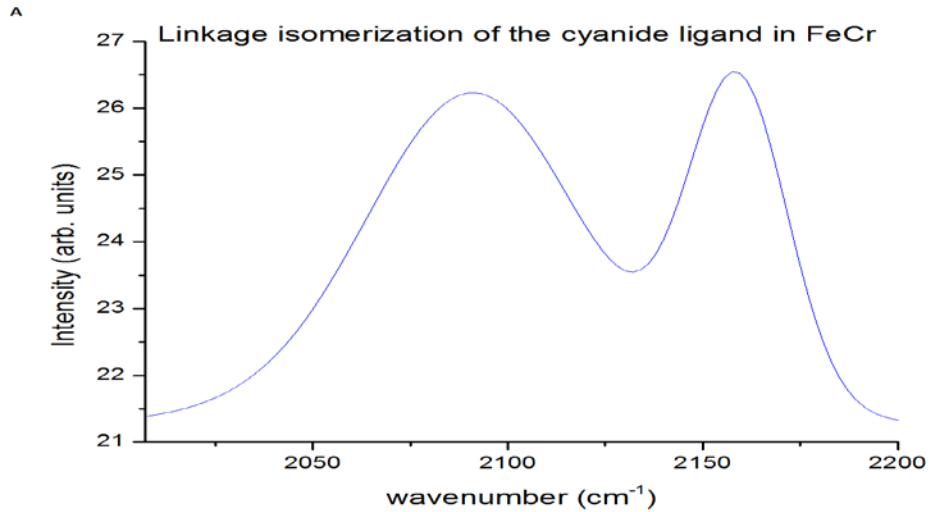

Cr
C
N
Fe

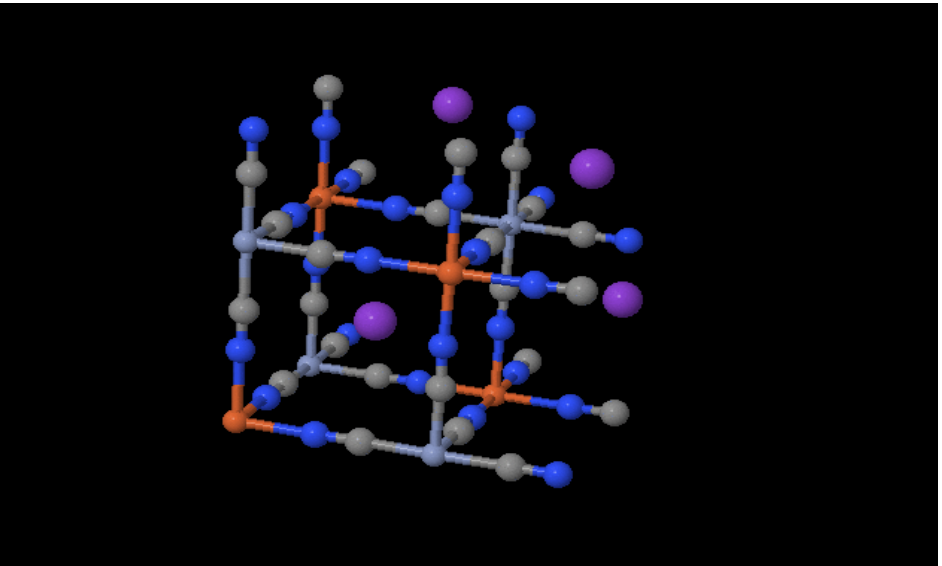

Variation of FeCr isomers' moment with given lattice
Fe moment (μ_B)
0
2
4
10.0
10.2
10.4
10.6
10.8
11.0
lattice constant (Å)
Fe (C-N)
Fe (N-C)


Cr
N
C
Fe

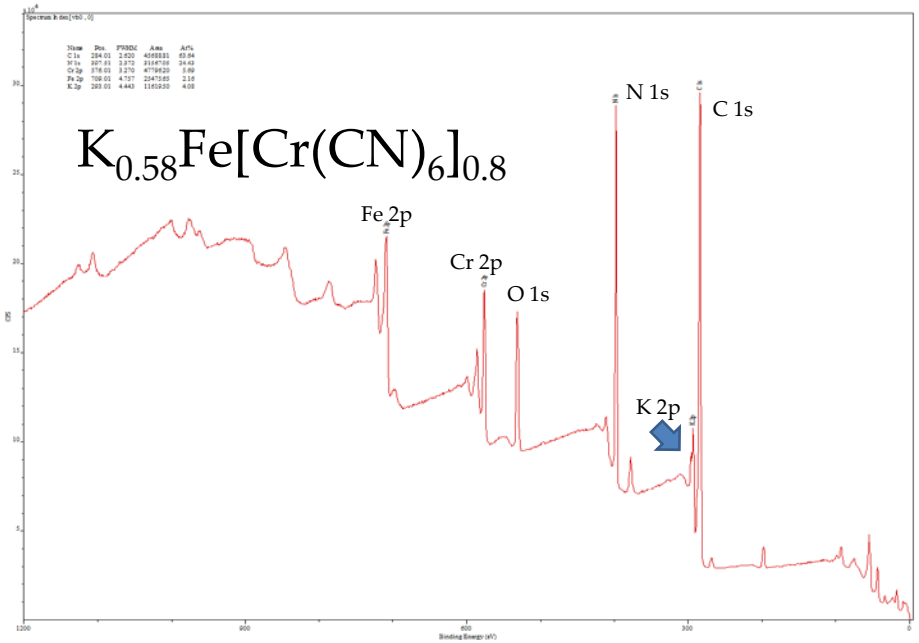
FeCr: Elemental Analysis

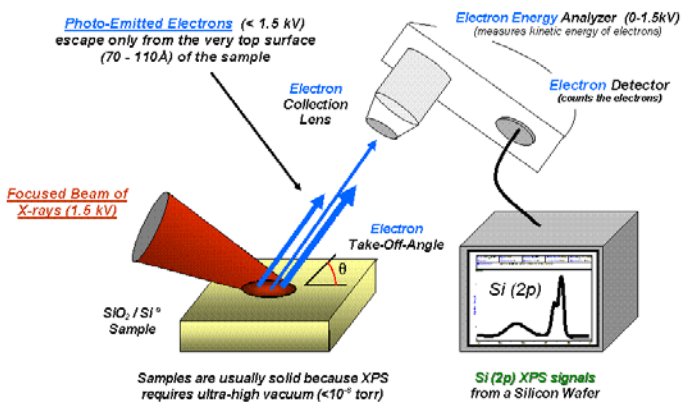
FT-IR



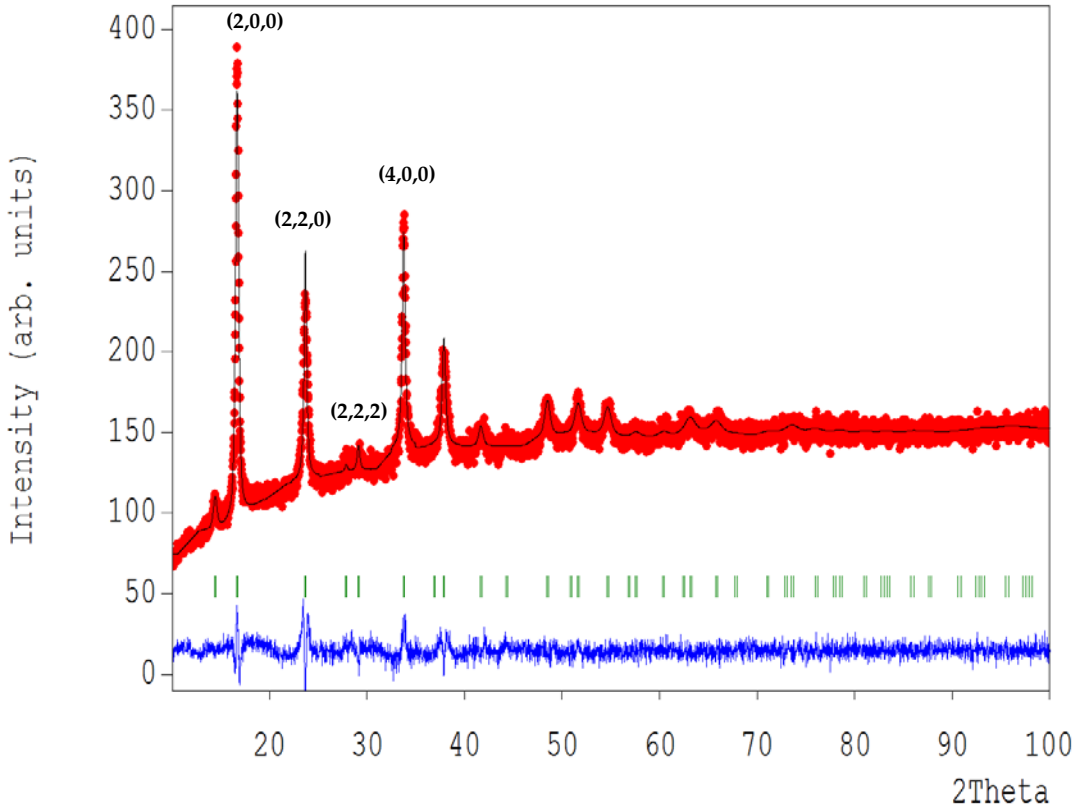


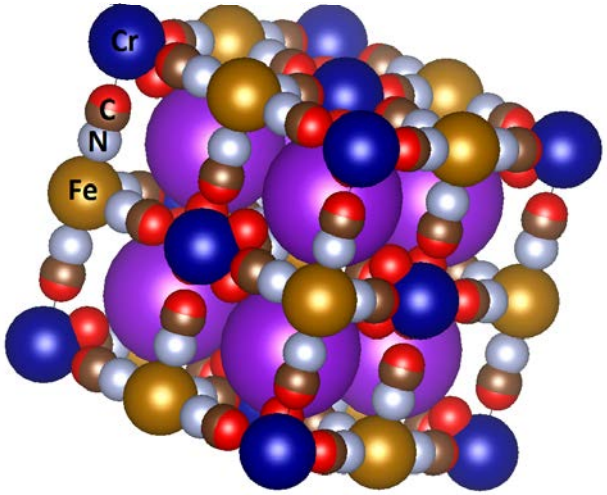
XPS





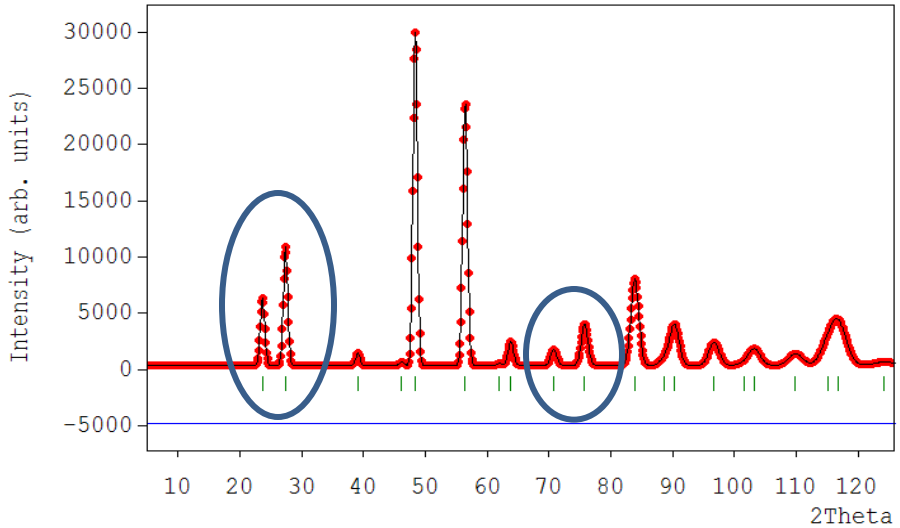
FeCr: XRD

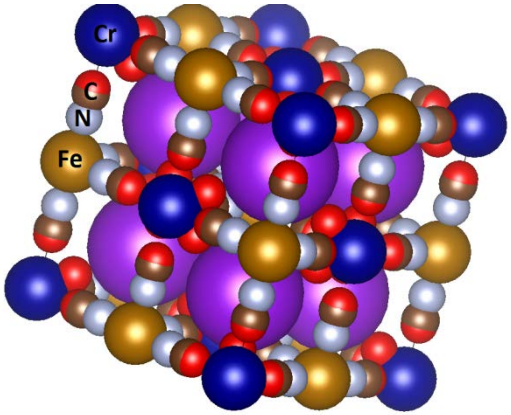


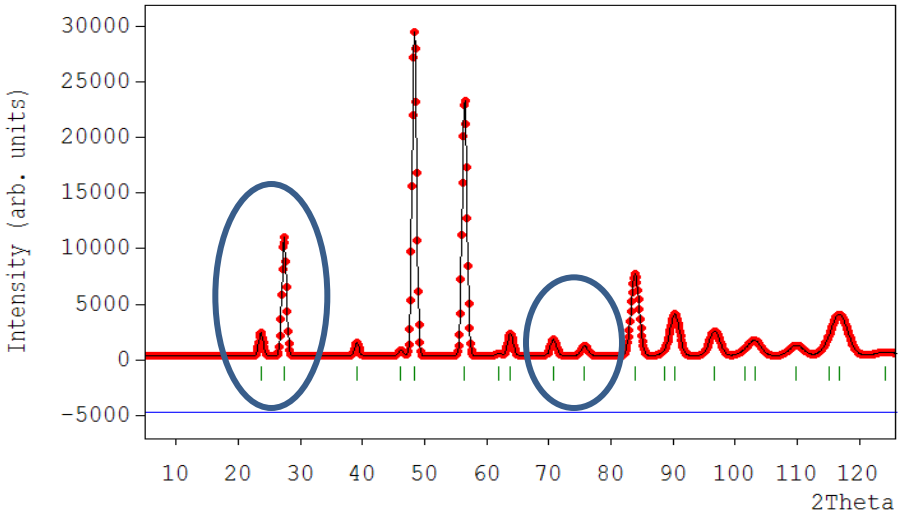


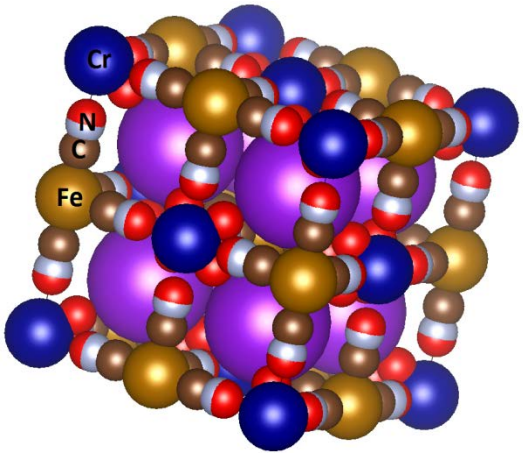
Element	X	Y	Z
Fe	0.5000	0.5000	0.5000
Cr	0.0000	0.0000	0.0000
C	0.0000	0.2685	0.5000
K	0.2500	0.2500	0.2500
N	0.0000	0.0000	0.3258

FeCr: Neutron Diffraction

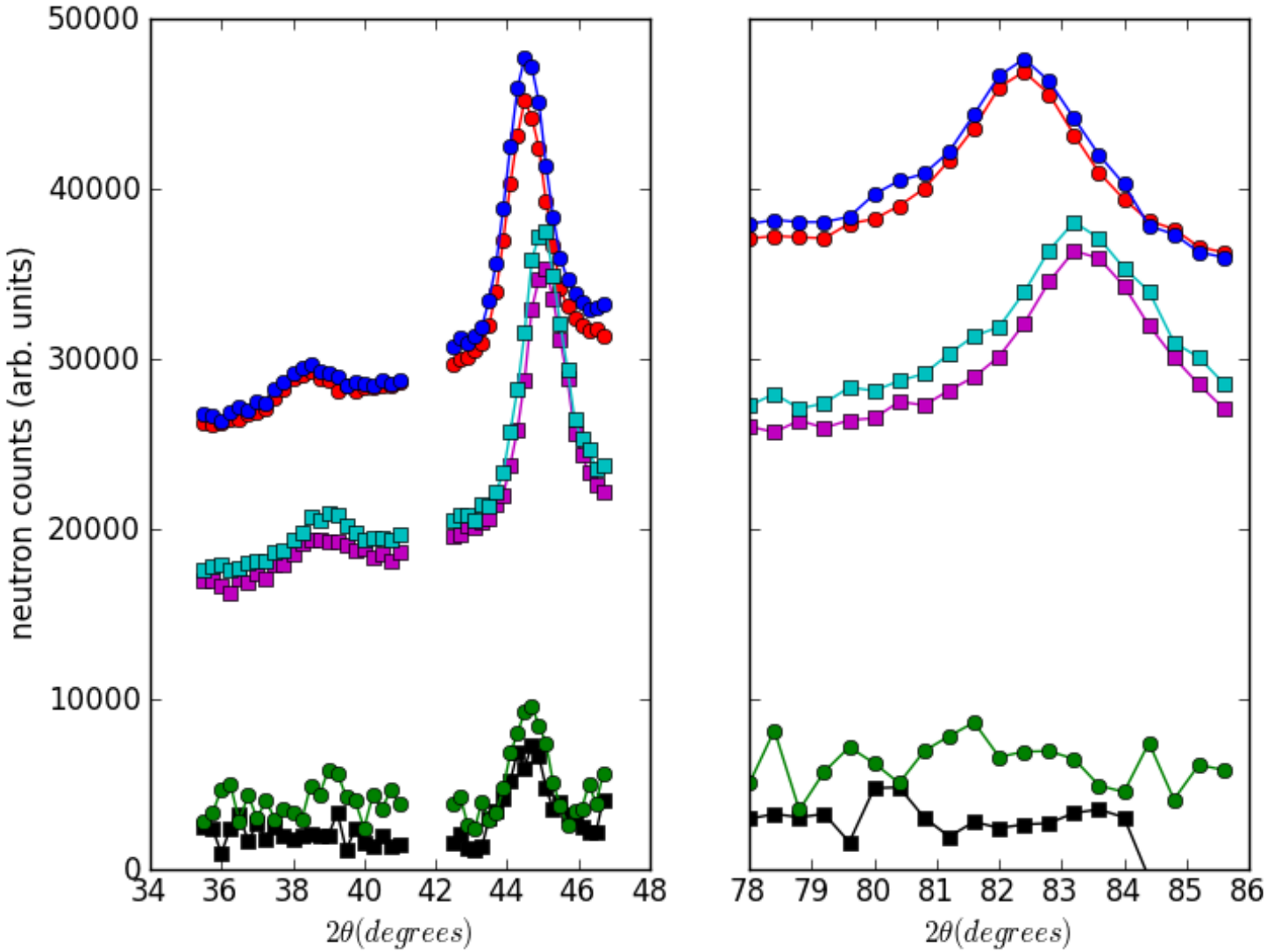




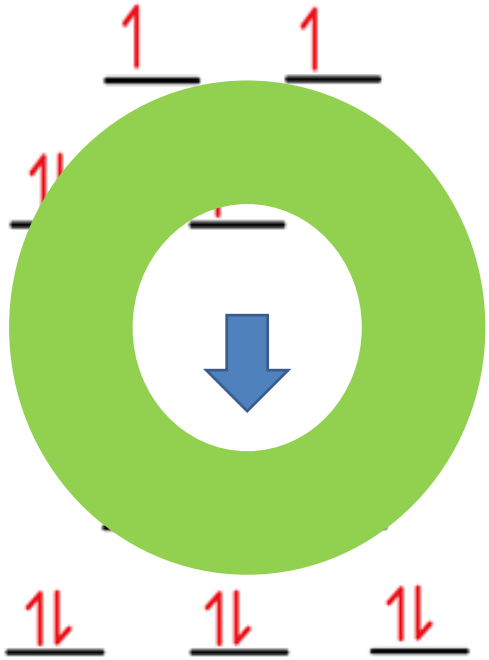




FeCr: Neutron Diffraction



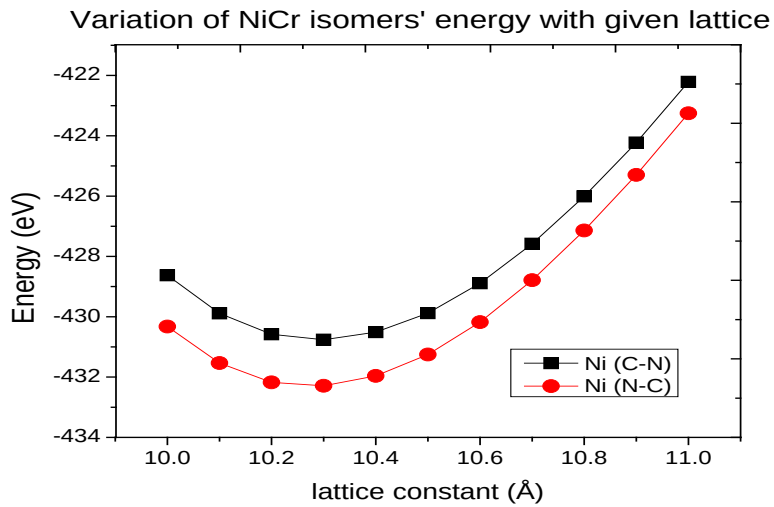
FeCr: Conclusion

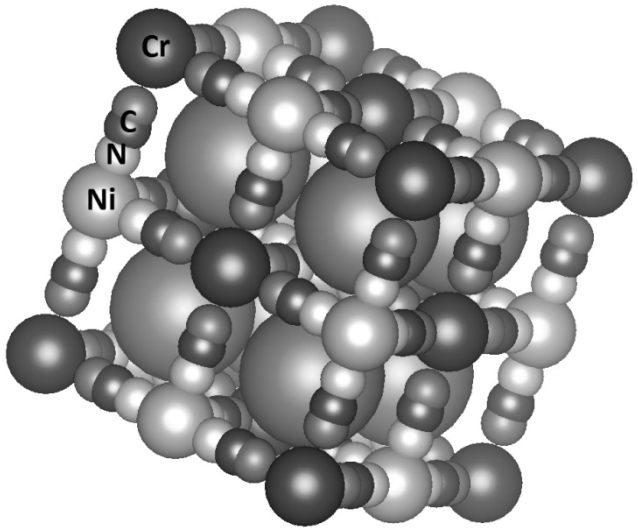


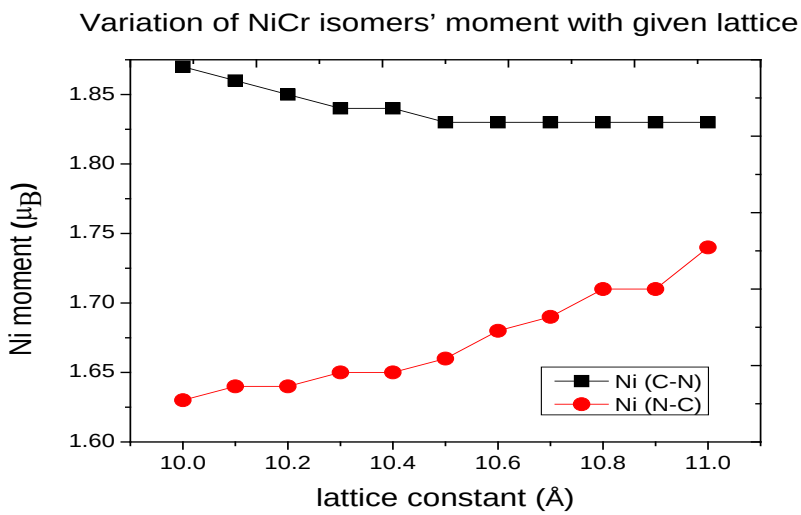
NiCr: Synthesis

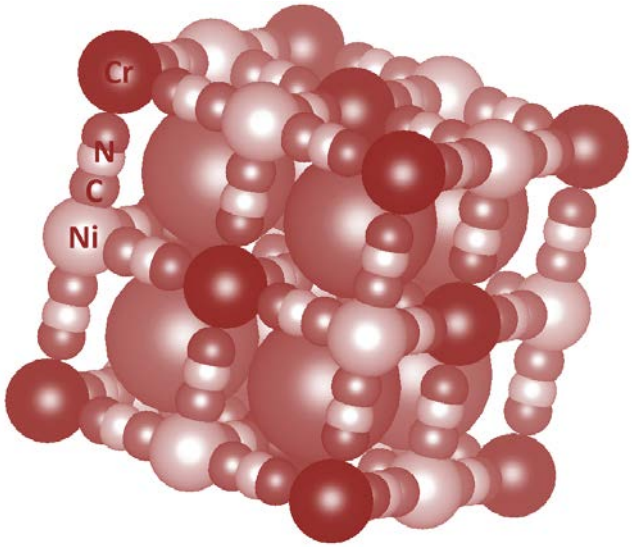
- $K_3Cr(CN)_6$
- $NiCl_2$
- KCl
- D_2O
- 60 °C
- Peristaltic Pump

NiCr: DFT


Variation of NiCr isomers' energy with given lattice
Energy (eV)
-422
-424
-426
-428
-430
-432
-434
10.0
10.2
10.4
10.6
10.8
11.0
lattice constant (Å)
Ni (C-N)
Ni (N-C)

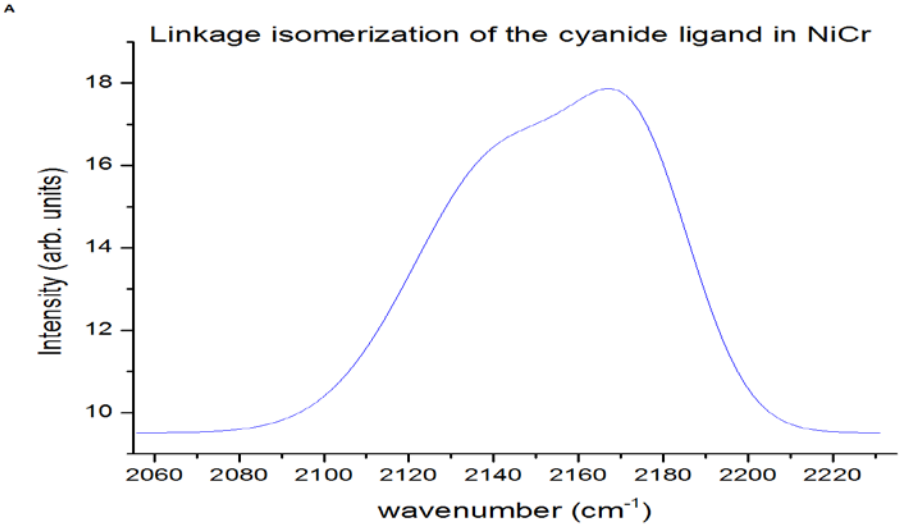

Cr
C
N
Ni

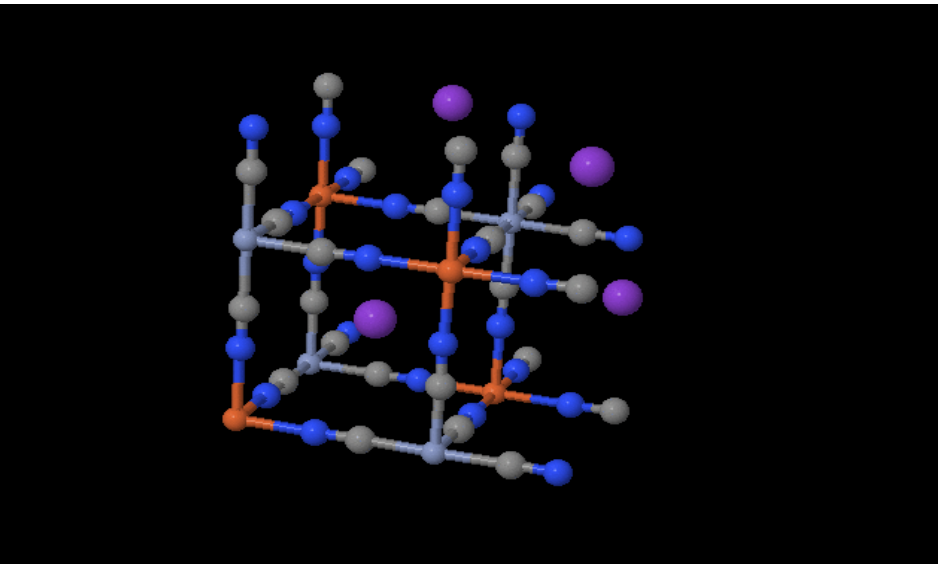

Variation of NiCr isomers' moment with given lattice
Ni moment (μ_B)
1.85
1.80
1.75
1.70
1.65
1.60
10.0
10.2
10.4
10.6
10.8
11.0
lattice constant (Å)
Ni (C-N)
Ni (N-C)


Cr
N
C
Ni

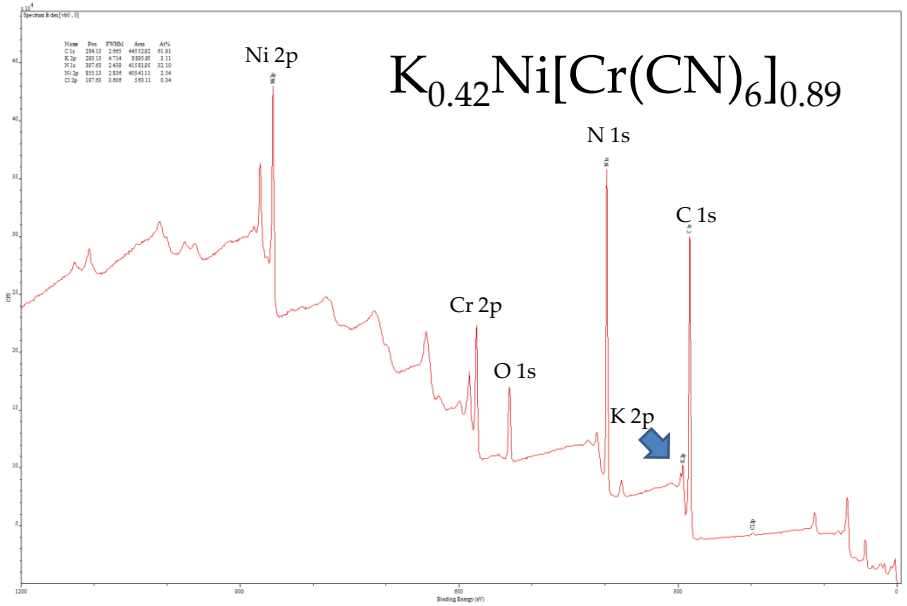
NiCr: Elemental Analysis

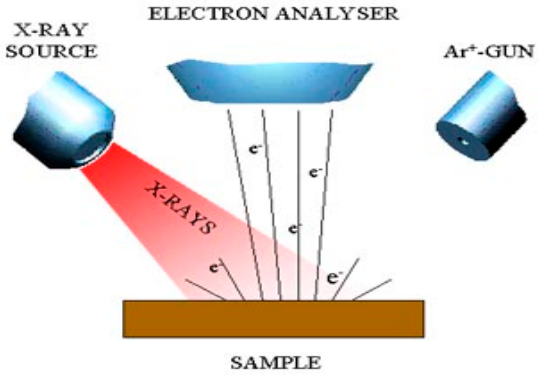
FT-IR



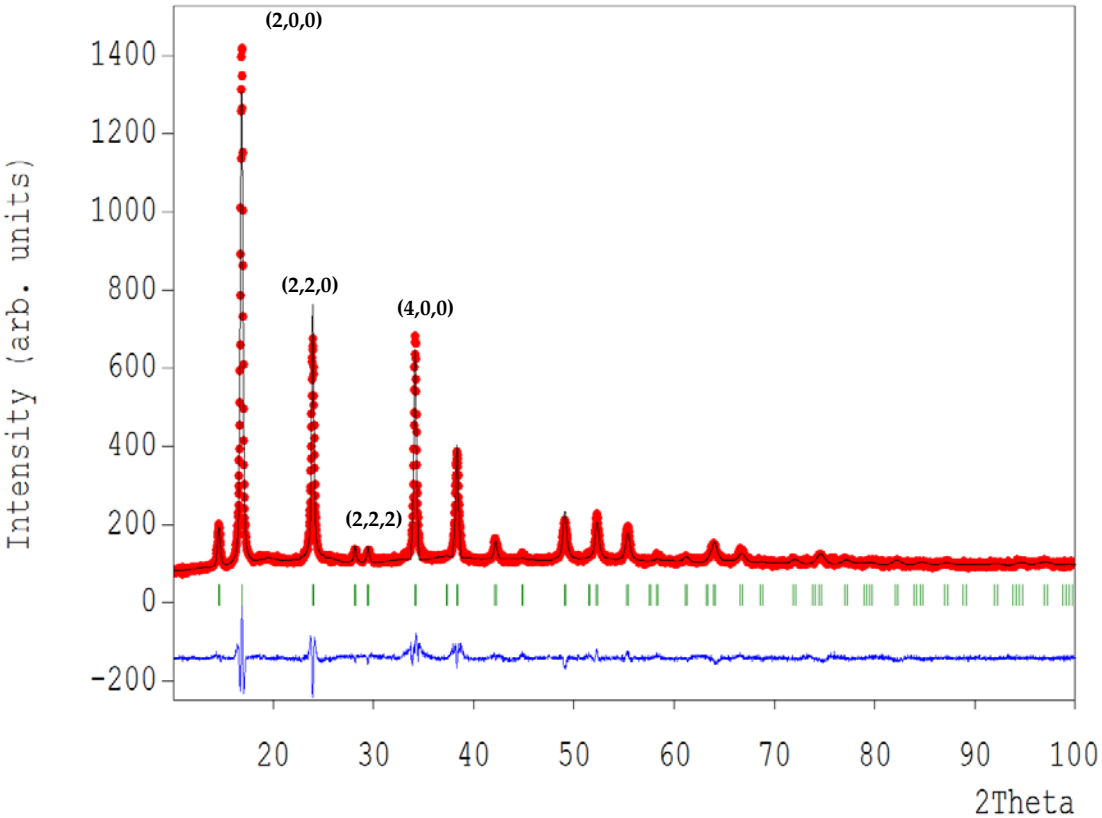


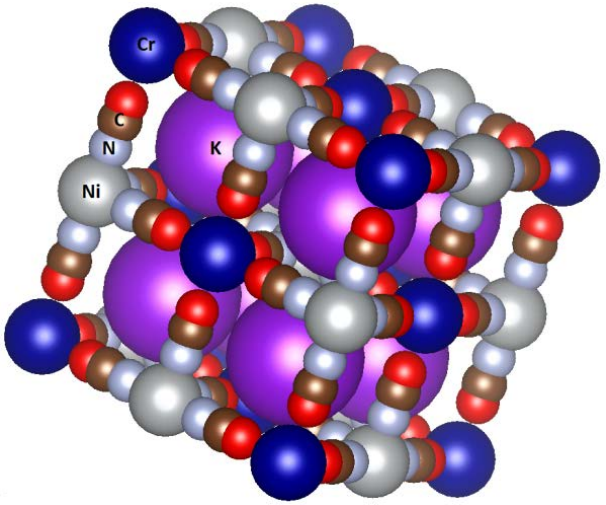
XPS





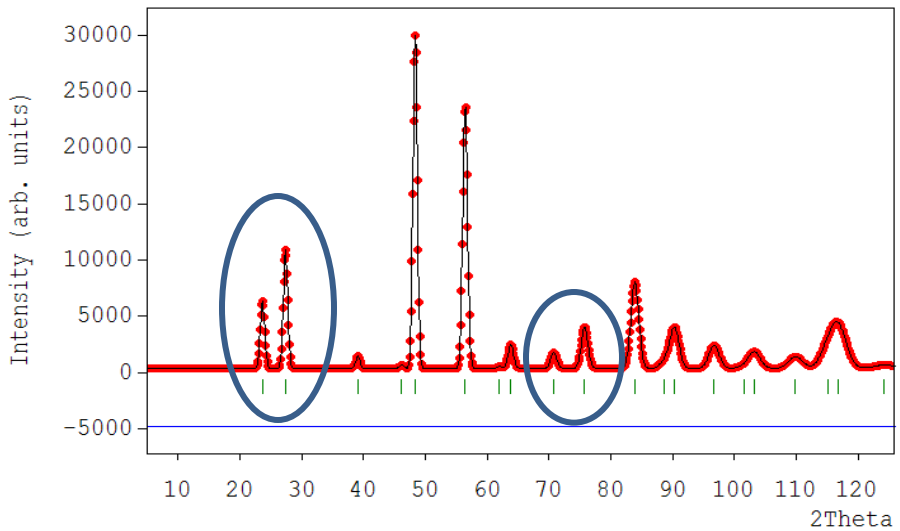
NiCr: XRD

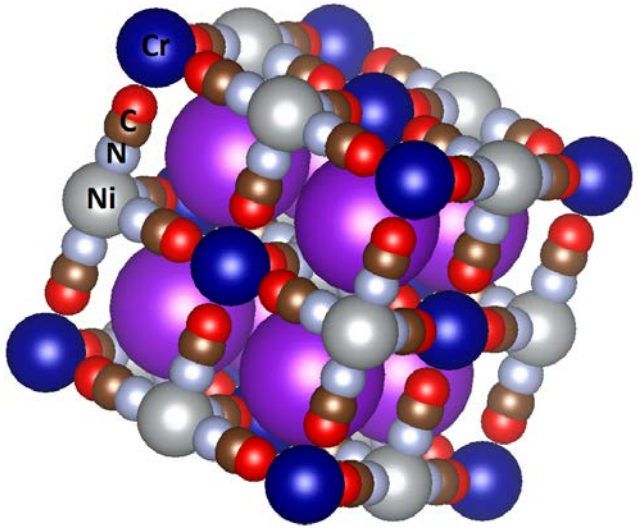


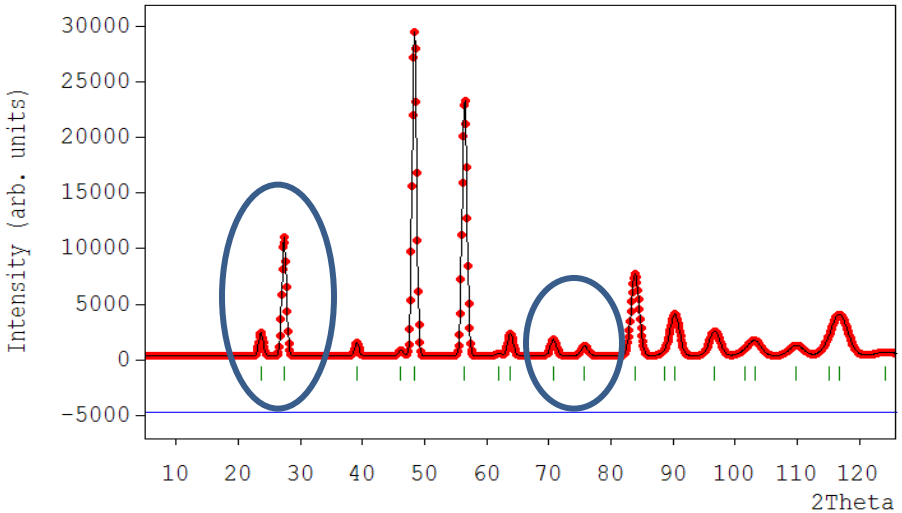


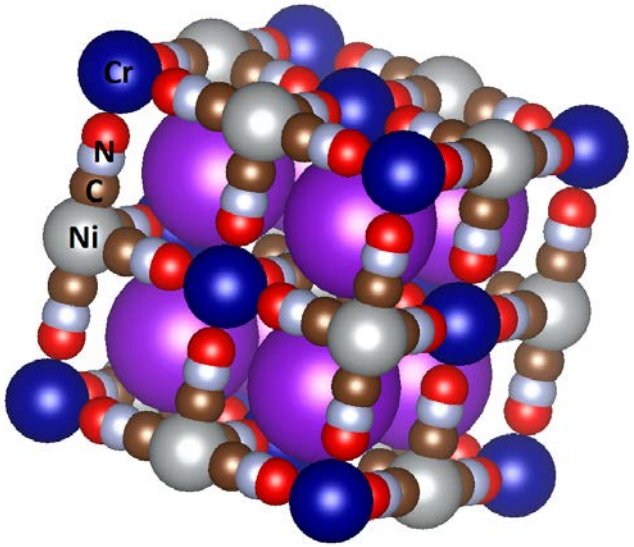
Element	X	Y	Z
Ni	0.0000	0.0000	0.5000
Cr	0.5000	0.0000	0.5000
C	0.0000	0.2413	0.5000
K	0.7500	0.2500	0.7500
N	0.0000	0.0000	1.3490

NiCr: Neutron Diffraction

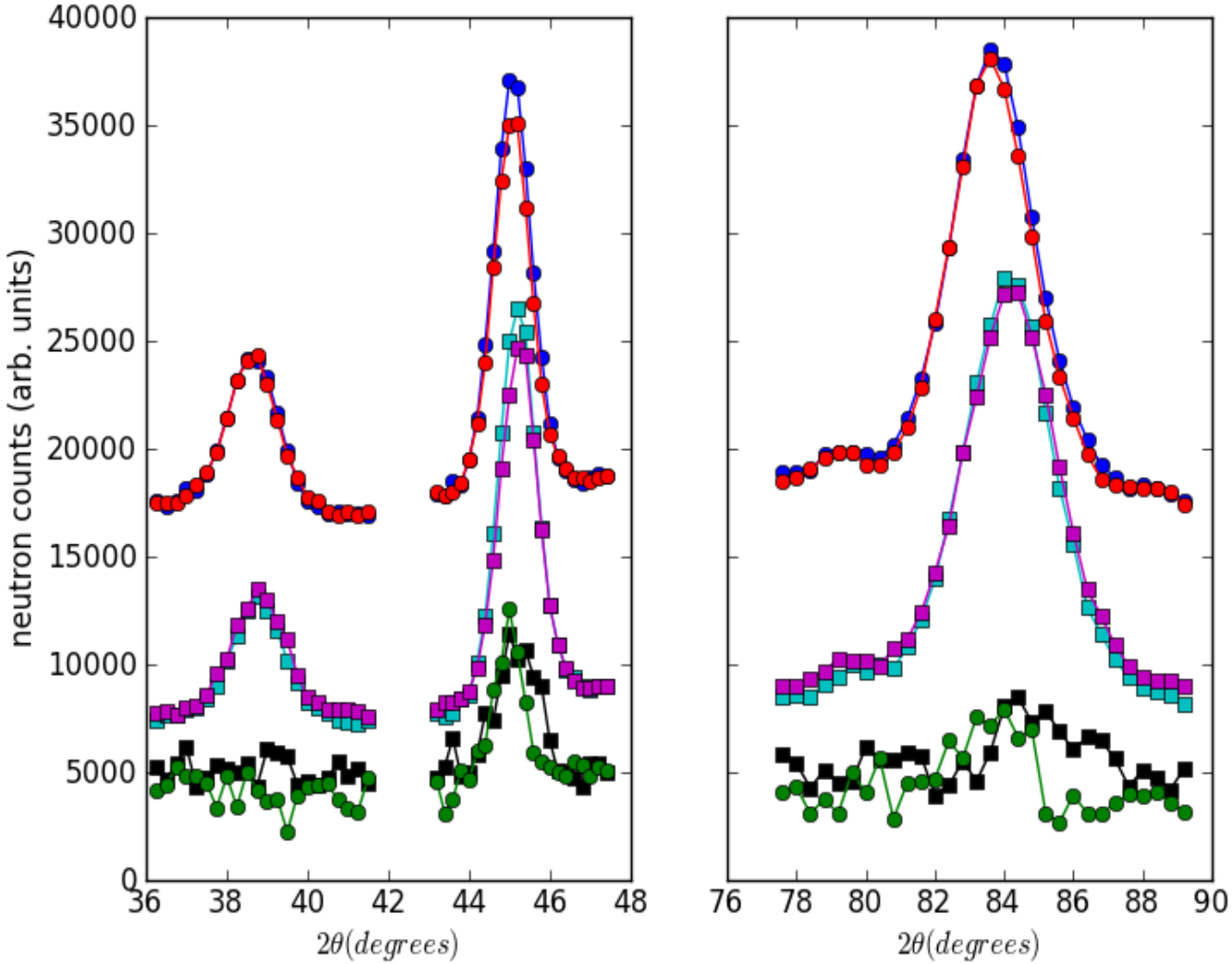




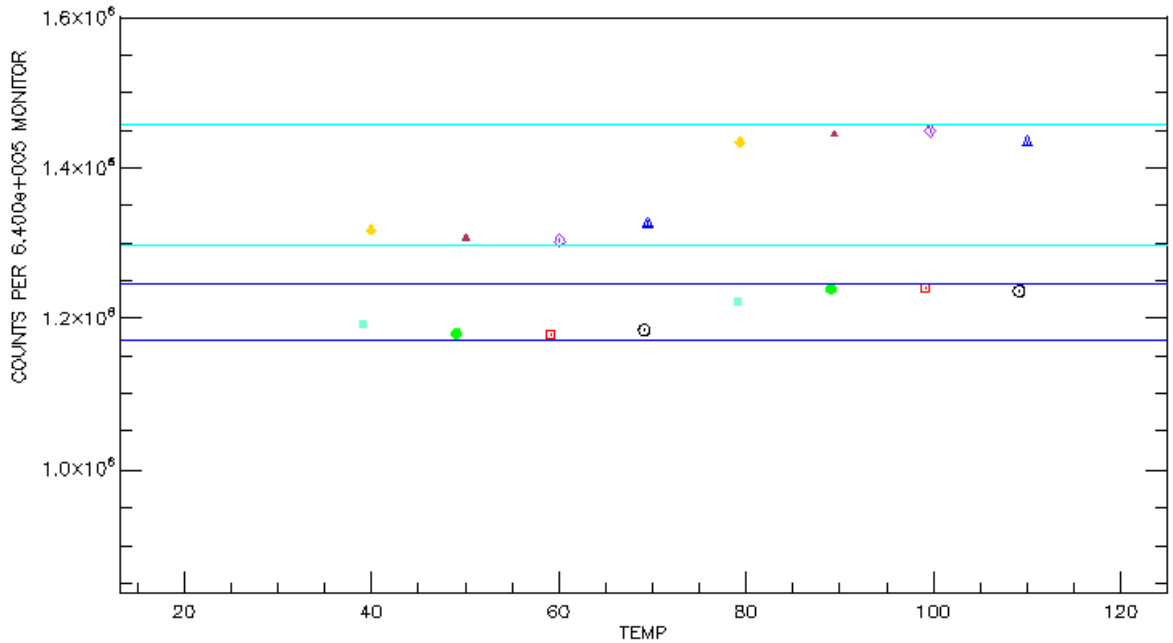


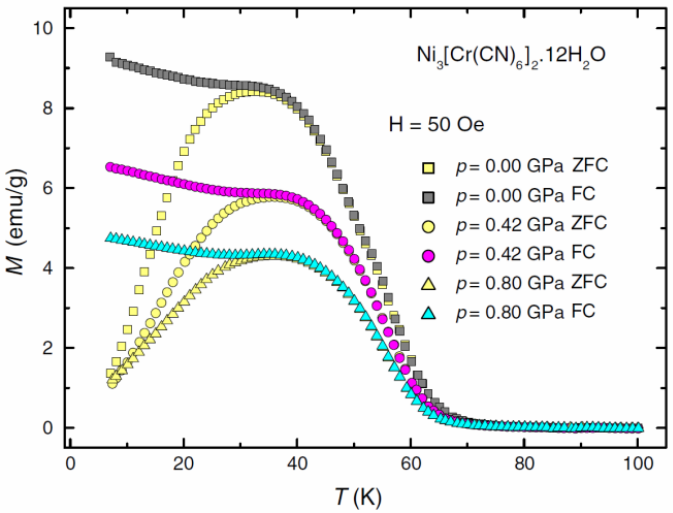


NiCr: Neutron Diffraction



NiCr: Polarized Neutron Diffraction





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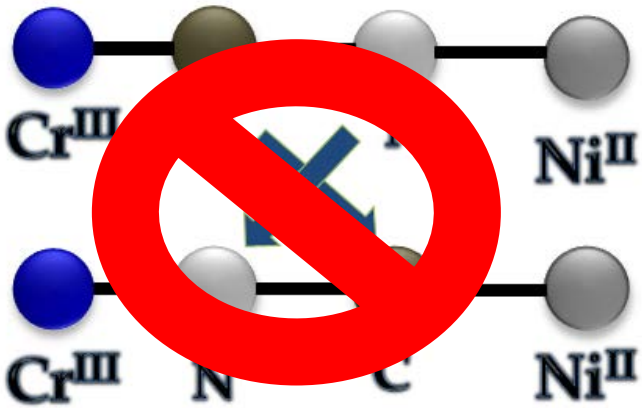
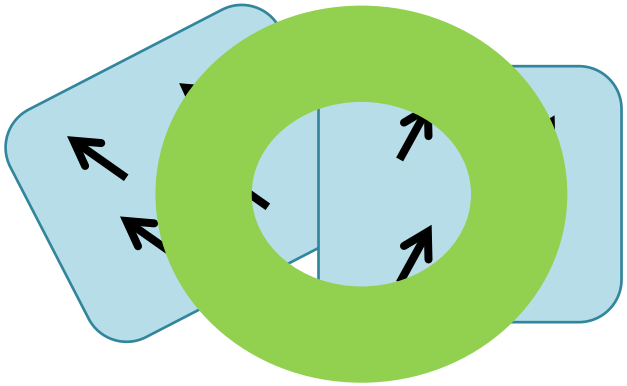
More depolarization at HIGH PRESSURE shows presence of domains effect.

NiCr: Conclusion

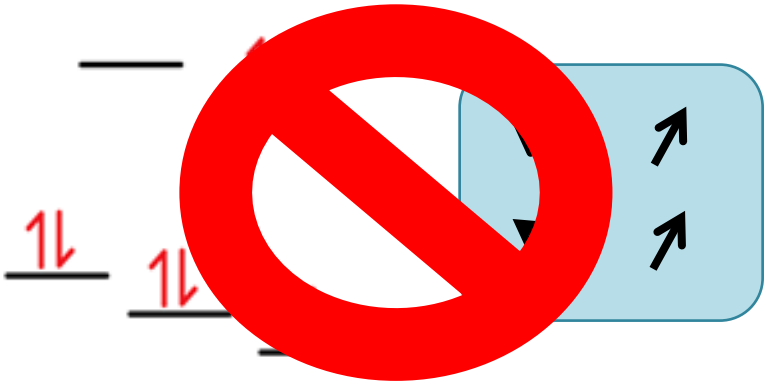
LI



Domain wall movement



Random spin-canting



The Big Kahuna!

- No LI in either sample.
- Domain wall movement (NiCr)
- Intrinsic spin-crossover (FeCr)

Acknowledgements

- Daniel Pajerowski
- Julie Borchers, Robert Shull, Terrell Vanderah
- Rob Dimeo, Dan Neumann
- NIST
- CHRNS
- NCNR
- And all of those who helped us in the process.

NIST Center for Neutron Research

NSF CHRNS Center for High Resolution Neutron Scattering NIST

It was a pleasure working with you guys!

Questions?

" The Great Wave off Kanagawa" by
Katsushika Hokusai *(c. 1829-32)*